

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 467 404 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **91112145.7**

(51) Int. Cl.<sup>5</sup>: **C09K 3/14, B24D 3/14**

(22) Date of filing: **19.07.91**

(30) Priority: **20.07.90 US 556069**

(43) Date of publication of application:  
**22.01.92 Bulletin 92/04**

(94) Designated Contracting States:  
**DE ES FR GB IT LU SE**

(71) Applicant: **NORTON COMPANY**  
**1 New Bond Street**  
**Worcester, MA 01615-0008(US)**

(72) Inventor: **Chen, Sy-Hwa**  
**7679 Brighton Way**  
**Salt Lake City, UT 84121(US)**  
Inventor: **Hansen, Jeffrey S.**  
**722 Timbercreek Way No. 417**  
**Salt Lake City, UT 84119(US)**

(74) Representative: **DIEHL GLAESER HILTL & PARTNER**  
**Patentanwälte Flüggenstrasse 13**  
**W-8000 München 19(DE)**

(54) **Diamond having multiple coatings, methods for their manufacture and use of same.**

(57) A diamond element having good bonding properties and a method for fabricating the diamond element in which a diamond substrate is coated by and bonded to a first layer of chromium carbide, a second layer containing titanium is bonded to said first layer, and a third layer of tungsten, or molybdenum deposited by a CVD technique utilizing metal halides, is bonded to said second layer. The second layer functions to protect the chromium carbide layer against attack by halide containing gas during the CVD deposition of the tungsten, or molybdenum.

**EP 0 467 404 A1**

Rank Xerox (UK) Business Services

The present invention relates to diamond with multiple coatings for improved retention in a matrix and methods for their manufacture.

Diamond is widely used in sawing, drilling, dressing, and grinding applications. The diamond is typically bonded to or mechanically held in a matrix of nickel, copper, iron, cobalt, or tin, or alloys thereof which is connected to a tool body. The matrix can also comprise a resin, such as phenol formaldehyde.

When the diamond is in the form of an abrasive grit, it is frequently mechanically bonded in the matrix with the matrix surrounding the grit and holding it in place. While simple and practical, mechanical bonds are relatively weak and the grit can be easily lost as the surrounding matrix is abraded away during use. Grit retention can be improved by embedding the grit deeply into the matrix leaving little grit exposure, but this decreases cutting efficiency. In a typical saw blade application, the average exposure of diamond grit is less than 20% of the total grit height. Grit loss can become a serious problem when the supporting matrix is worn down such that over one-third of the grit is exposed. The average lifetime of such cutting tools is decreased as up to two-thirds of the original diamond grit are prematurely lost.

From U.S. Patent 3,871,840, it is known that a tungsten coating deposited on a diamond particle enhances the ability of a matrix material, such as bronze or a bronze alloy, to adhere to the diamond particle and thereby to retain the particle in a tool during the use of the tool in abrading, cutting or grinding use.

Additionally, in an attempts to improve grit retention, it has been known to coat diamond particles with carbide forming transition metals such as titanium or zirconium. The coating's inner surface forms a carbide with the diamond. A second layer of a less oxidizable metal, such as nickel or copper, can then be applied to protect the inner layer from oxidation.

Tensile testing of double layer coated diamond having an inner layer such as chromium and an outer layer such as nickel shows that fracturing occurs at the interface between the inner and outer metal layers. This suggests that nickel does not alloy or otherwise bond well with the underlying carbide and that double layer coated grits may not significantly improve overall grit retention. Bonding can also be weakened by oxidation of the inner chromium layer during the nickel coating process.

It is also known to coat diamond particles with titanium, manganese, chromium, vanadium, tungsten, molybdenum or niobium by metal vapor deposition. It has been found, however, that these carbide formers do not bond strongly enough to the diamond crystals to improve their grit retention

for many high stress applications, or they are susceptible to oxidation. As discussed above, the outer metal layers used to protect inner layers from oxidation do not adequately bond to the inner layer.

As illustrated in commonly owned US Patent No. 5,024,680 the disclosure of which is hereby incorporated by reference, attempts have been made to further improve the bonding strength between a matrix and diamond particles by first coating the diamond particles with chromium and then depositing a coating of tungsten on the chromium by a chemical vapor deposition technique. A typical CVD technique is to levitate or tumble the chrome coated diamond in a vapor. The vapor is typically composed of tungsten hexafluoride. It has been discovered however, that while favorable results have been achieved by this process, there is an unfortunate tendency for the fluorine containing gas to react detrimentally with the chromium containing coating to produce chromium fluoride. Therefore, for CVD depositions utilizing tungsten hexafluoride, the strength of the layered system is limited by the presence of the chromium fluoride between the chromium carbide and the tungsten layer.

It is therefore an object of the present invention to provide an improved retention of diamond in a matrix. This object is solved by a diamond element according to independent claim 1, its use according to claim 6, an article of manufacture according to independent claim 7 and a method for producing a diamond element according to independent claim 12. Further details and features are evident from the dependent claims and the description. The claims are intended to be understood as a first non-limiting approach of defining the invention in general terms.

It has been discovered that the retention of diamond may be enhanced by first depositing a layer of chromium on the material to form a chrome carbide layer, then depositing a layer of titanium on to the chrome carbide layer. The titanium containing layer is then nitrided to form a layer containing titanium nitride, and finally, a layer of tungsten, or molybdenum is deposited on top of the titanium nitride containing layer. The intermediate layer containing titanium nitride not only bonds exceptionally well to both the underlying chromium carbide and to the overlying tungsten, but it forms a protective barrier against attack by the halide (fluorine for example) containing gas on the chromium carbide during the tungsten deposition process.

In accordance with the process of the present invention, diamond is coated with a first metal coating layer comprising chromium. The chromium is reacted with the diamond to produce a chromium carbide containing layer which is chemically

bonded to the underlying diamond. Investigations have revealed that coating thicknesses of at least .05  $\mu\text{m}$  is preferable to produce desirable results.

Following the deposition of the chromium layer and formation of the chromium carbide, a titanium containing layer is formed on the exterior of the chromium carbide. The titanium is then passivated against reaction with a halide containing gas (such as fluorine) by nitriding the titanium. Once nitrided, a coating of a transition element such as tungsten or molybdenum, preferably tungsten, is placed on top of the titanium nitride by a chemical vapor deposition technique which exposes the particle to halide (fluorine) containing gas.

A variety of alternatives are possible for the initial deposition of the chromium layer. A first alternative is coat the diamond surface on which the chromium is to be deposited by metal vapor deposition ("MVD"). In MVD, a layer of fine chromium powder is mixed with the diamond to be coated and then heated in a furnace for an hour or more at elevated temperatures on the order of 600 - 700°C and under an approximate  $10^{-5}$  torr vacuum. This treatment causes the chromium powder to vaporize and to redeposit on the surfaces of the diamond in an even layer over the surface of the diamond. During the process, agitation may be applied to prevent the particles from adhering to one another. Chromium powder particle sizes on the order of 325 grit size are preferred. Conditioning the chromium powder with hydrogen chloride assists in the coating process. One may also perform this coating process in a methane gas atmosphere or other non-oxidizing atmosphere such as argon or hydrogen. Other deposition methods can be used to apply the first chromium layer.

As another alternative, one may apply the chromium coating by mixing the diamond and the chromium powder with a salt bath that contains, for example NaCl,  $\text{CaCl}_2$ , and KCl. This combination is then soaked at about 650°C or above for about five minutes to dissolve the chromium in the molten salt bath and the chromium forms a layer on the diamond crystals.

As previously suggested, it is believed that the entire chromium layer chemically reacts with the carbon of the diamond particle to form chromium carbide ( $\text{Cr}_3\text{C}_2$ ), bonded to the diamond. It is believed that this bond is an atom to atom bond between the carbon of the diamond and the carbide layer.

The preferred range of thickness for the chromium layer is between 0.05 to 1  $\mu\text{m}$ , while a thickness of up to 5  $\mu\text{m}$  is acceptable. 0.05 to 0.30  $\mu\text{m}$  is most preferred. If the metal/carbide layer is too thin, subsequent metal coatings could diffuse to

the surface of the diamond, displacing the chromium and forming weaker bonds with the diamond. 0.05  $\mu\text{m}$  has been found to be about the minimum coating thickness which ensures a continuous chromium carbide coating which is adequate for bonding.

Utilizing a diamond grit with a nominal diameter of 500  $\mu\text{m}$  mixed with a 99.8 percent pure chromium metal powder having an iron contamination of less than 0.1% (available from Cerac, Inc with product designation C-1221), it was found that an MVD process of from four to six hours at 720°C and  $10^{-5}$  torr, yielded chromium coatings of at least 0.05  $\mu\text{m}$ . Two hours of MVD at 770°C yielded coatings of between 0.10 and 0.40  $\mu\text{m}$ . Two hours of MVD at 820°C and 870°C yielded coatings of between 0.03 and 0.50  $\mu\text{m}$  and 0.50 to 0.80  $\mu\text{m}$ , respectively. One hour of MVD at 920°C yielded coatings of about one  $\mu\text{m}$  in thickness.

In the formation of the next, titanium containing layer, a titanium coating is applied in a similar MVD process at 900°C for six hours under a  $10^{-5}$  torr vacuum. The titanium powder was mixed in a 1:1 weight ratio with diamond; 0.1 mls of concentrated HCL had been added per 3.0 gms titanium and then dried prior to mixing. Preferably, the titanium is deposited to a thickness equal to or exceeding 0.1  $\mu\text{m}$ . It is believed that thicknesses up to 10  $\mu\text{m}$  are feasible, while thicknesses greater than 10  $\mu\text{m}$  are expected to crack under coating induced stresses. Upon formation of the titanium containing layer, the coated grit is then heated at about 1000°C in a nitrogen ( $\text{N}_2$ ) atmosphere for two hours. This heating process causes the outermost portions of the titanium containing layer to combine with the nitrogen to form titanium nitride. Alternatively, the titanium may be deposited by a physical vapor deposition (sputtering) process or by a CVD process.

Finally, the third, outermost tungsten or molybdenum containing coating layer may be applied by a chemical vapor deposition or a physical vapor deposition technique. Metal vapor deposition is not preferred, however, because the high temperatures required in the process would tend to degrade the diamond.

The most preferred method for applying the tungsten layer is by chemical vapor deposition which involves the reduction of a metal compound (such as tungsten hexafluoride) on the surface of the diamond. See, for example, U.S. Patent No. 3,757,878, to Wilder. CVD is preferred because of the ease with which a large number of pieces of diamond can be evenly coated and the relatively low temperature that can be used to deposit the tungsten. In the process of the invention, CVD is

\* 1 torr = 1.3 mbar

typically performed at 700°C, and 7 torr, in a reducing atmosphere for between 15 and 90 minutes. Tungsten is the preferred material for this outermost layer since tungsten bonds favorably with typical matrix materials such as cobalt and nickel and commonly used infiltration alloys such as Cu-Zn-Ni. The tungsten from this outermost layer may bond with such matrix materials by diffusion and the formation of a solid solution with the matrix material. There can also be intermetallic bonding with the matrix, depending on the matrix.

The tungsten layer is preferably between 5 - 50 µm thick, with coatings up to 30 µm being more preferred. Thinner coatings may be adequate depending in part on the methods and conditions of application. For example, CVD can yield a somewhat columnar tungsten coating which may be permeable to liquid alloy. The coatings must therefore be thick enough to adequately protect the inner metal layer from subsequent undesirable reactions.

#### EXAMPLE

Twenty pieces of 1/2 carat single crystal diamonds were mixed with 6 gms of a 0.044mm (325 mesh) chromium powder. 200 gms of the chromium powder had been previously treated with 72cc of water and 6cc of 36% HCl for one hour, then drained and dried. The powder and diamond mixture was then processed in a tube furnace at 800°C for one hour in a methane atmosphere. This procedure produced a uniform chromium carbide layer.

Next, the chromium carbide coated diamond was mixed with a 0.044 mm (325 mesh) titanium powder that had been treated with HCl in a manner similar to that described above for chromium. The titanium and diamond mixture was then processed in the high vacuum furnace at 900°C for six hours. During this time, the furnace was maintained with a vacuum of about 10<sup>-5</sup> torr. The Ti/Cr coated diamond was then placed in a nitrogen (N<sub>2</sub>) atmosphere at 1000°C for two hours to convert the titanium containing layer at least partially into titanium nitride (TiN). While not wishing to be bound by any particular theory, it is believed that the titanium coating interacts with the carbon of the chromium carbide layer to produce an interior titanium carbide layer immediately adjacent to the chromium carbide. There may also be an intermediate, transition layer comprising titanium carbide/nitride (Ti(C<sub>x</sub>N<sub>y</sub>)) between the titanium carbide and the titanium nitride portions of this coating.

Finally, the Cr/Ti coated diamond was placed in a CVD chamber and coated with tungsten to a thickness of 30 µm. It is believed that a thickness of 30 µm is necessary for the tungsten layer to

effectively act as a diffusion barrier to the migration of elements found in common infiltration binders (such as Cu/Ni base alloy) that are commonly utilized in subsequent procedures for bonding the diamond into a tool shank. Where hot pressing is the mounting technique to be employed, rather than infiltration bonding, the tungsten layer may be as thin as 5 µm.

The above described coated half carat diamond was incorporated in the working end of the shank of a grinding wheel truing tool. The diamond was packed in tungsten powder which was then infiltrated with a copper-zinc-nickel alloy at 1000°C for 20 minutes in an ammonia atmosphere. When tested, the diamond was retained in the tool even after the shank in which it was mounted was abraded below the largest girth of the diamond. Un-coated diamonds or diamonds coated with the chromium containing layer and tungsten in similar conditions were plucked out of their tools when the shanks were abraded to the same degree.

#### Claims

1. A diamond element having good bonding properties, comprising:
  - a. a diamond substrate;
  - b. a first layer bonded to said diamond substrate;
  - c. a second layer bonded to said first layer; and
  - d. a third layer bonded to said second layer, said first layer including chromium carbide said third layer including a transition element and said second layer including an element other than chromium or said transition element where said transition element is tungsten, or molybdenum.
2. The diamond element as recited in claim 1 wherein said second layer comprises a compound resistant to halide attack.
3. The diamond element as recited in claim 2 wherein said second layer comprises a titanium compound, wherein said titanium compound preferably comprising titanium nitride.
4. The diamond element as recited in one of the preceding claims, wherein said third layer is deposited by a chemical vapor deposition process having a halide as a source material.
5. The diamond element as recited in one of the preceding claims in which the layers are chemically bonded.
6. Use of the diamond element of one of the

preceding claims in an article of manufacture, especially a cutting tool.

7. An article of manufacture, especially an abrasive tool, containing a firmly secured diamond element, said article comprising:
  - a. a diamond substrate;
  - b. a first layer bonded to said diamond substrate;
  - c. a second layer bonded to said first layer;
  - d. a third layer bonded to said second layer; and
  - e. a body bonded to said third layer, said first layer including chromium carbide, said third layer including a transition element and said second layer including an element other than chromium or said transition element where said transition element is tungsten or molybdenum.
8. The article of manufacture of claim 7 wherein said first to third layers are chemically bonded.
9. The article of manufacture as recited in claim 7 or 8 wherein said second layer comprises a compound resistant to halide attack preferably a titanium compound, wherein said titanium compound preferably comprises titanium nitride.
10. The article of manufacture as recited in one of claims 7 to 9, wherein said third layer is deposited by a chemical vapor deposition process having a halide as a source material.
11. The article of manufacture as recited in one of claims 7 to 10 wherein said body comprises a tungsten matrix infiltrated with a copper-zinc-nickel alloy.
12. A method for producing a diamond element capable of being securely bonded to a substrate, the method comprising the steps of:
  - a. depositing a first layer on said diamond element;
  - b. depositing a second layer on said diamond element; and
  - c. depositing a third layer on said diamond element, said first layer including chromium carbide, said third layer including a transition element and said second layer including an element other than chromium or said transition element where said transition element is tungsten or molybdenum.
13. The method as recited in claim 12 wherein said step of depositing a third layer comprises the step of depositing said tungsten or molyb-

denum in a chemical vapor deposition process in the presence of halide gas and wherein said second layer comprises a compound resistant to attack by said halide gas.

14. The method as recited in claim 12 or 13 wherein said step of depositing a second layer includes the step of depositing a layer of material resistant to attack by halides.
15. The method as recited in one of claims 12 to 14, wherein said step of depositing a second layer includes the steps of depositing a layer of titanium and passivating said titanium against attack by halides.
16. The method as recited in claim 15 wherein said passivating step includes nitriding said titanium.



European  
Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 11 2145

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y,D	WO-A-9 005 170 (NORTON) * Claims 1-4; page 15, lines 14-26; page 18, lines 1-20 *	1-16	C 09 K 3/14 B 24 D 3/14
Y	US-A-4 184 853 (OTOPKOV) * Claims 1,8,12,13 *	1-16	
A	FR-A-272 197 (UNITED TECHNOLOGIES CORP.) * Claims 1,5; abstract *	1-16	
A	FR-A-1 574 515 (BALZERS) * Abstract, points 1,3,7 *	1-16	
A	US-A-3 826 630 (ROY) * Claims 1,2 *	1-16	
A	FR-A-2 169 573 (CHRISTENSEN DIAMOND) * Claims 1,4,5,6 *	1-16	
A	DERWENT FILE SUPPLIER JAPS, Derwent Publications Ltd, London, GB; & JP-A-58 110 495 (MATSUSHITA) * Whole abstract *	1-16	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 K
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 22 October 91	Examiner NICOLAS H.J.F.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &amp;: member of the same patent family, corresponding document</div>			